Materials Science and Engineering C 30 (2010) 758–762

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Biologically formed hollow cuprous oxide microspheres

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ARTICLE INFO

Article history:
Received 30 August 2009
Received in revised form 10 January 2010
Accepted 15 March 2010
Available online 27 March 2010

Keywords:
Biomimetic synthesis
X-ray diffraction
Hollow structure
Semiconducting materials

ABSTRACT

Hollow cuprous oxide (Cu_2O) microspheres with a diameter of ca. 1.8 μm are prepared by using yeast as template. The possible mechanism for the formation of the hollow Cu_2O spheres is revealed. The biotemplated sample is investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet–visible (UV–vis) absorption spectra. The sample consists of the crystalline Cu_2O microspheres with diameters of about 59.5 nm and lattice parameter of 4.264 Å. The observed optical band gap of the product indicates that the blue–shift effect occurs, which is attributed to the hollow Cu_2O microspheres.

1. Introduction

Hollow structures have attracted considerable attention because of their potentially numerous applications in catalysts, controlled delivery, lightweight fillers, low-dielectric materials, photonic crystals, confined-space chemical reactors, and biomedical diagnosis and therapy [1–3]. Among various synthesis approaches, template-directed synthesis methods have been demonstrated to be effective for preparing hollow structures. Various methods using hard templates or soft templates have been extensively investigated [4–9]. Among template-directed synthesis strategies, hard template synthesis has obtained great success for fabricating hollow microspheres. To date, a number of metal oxide hollow microspheres have been prepared by using silicon dioxide (SiO_2), polystyrene (PS) and carbonaceous polysaccharide microspheres as the templates [5,10,11]. In spite of these successes, there still exist some problems to be overcome. The traditional template requires surface modification, which is fussy and complicated. Moreover, traditional template approach is time consuming, expensive and probably environment-unfriendly [12]. Thus, it is highly recommended to develop a biotemplated synthesis for the preparation of inorganic hollow microspheres.

Cu_2O is a p-type semiconductor that has potential applications in solar energy conversion [13], catalysis [14], lithium ion batteries [15], biosensor [16] and so on. Although Cu_2O microspheres with hollow structure have been successfully synthesized by traditional chemical template [17–19], the biomimetic synthesis of hollow cuprous oxide microsphere has not been reported.

Recently, it becomes popular to synthesize inorganic hollow spheres by using microorganisms as template. Zhou et al. fabricated ZnO hollow spheres by employing lactobacillus as template [20]. Bai et al. prepared the Cr_2O_3 hollow particles using yeasts as template [21]. To the best of our knowledge, both dead and living cells are able to bind metal cations through electrostatic interaction because of their active biomolecules of the cell walls [22–27]. No surface modification or activation steps are required and the microorganisms are abundant in nature and can be easily obtained in large amounts. Consequently, the microorganisms are good candidates as template for preparing inorganic hollow spheres.

In this paper, we report the preparation approach of Cu_2O hollow microspheres using yeast cells as template and their characterizations by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and ultraviolet–visible (UV–vis) spectroscopy. We propose a possible mechanism for the formation of the Cu_2O hollow spheres. We evaluate the optical properties of the final products.

2. Experimental

2.1. Materials

In this work, copper sulfate ($CuSO_4 \cdot 5H_2O$, 98%, Shanghai Reagent No. 1 Plant), sodium hydroxide (NaOH, 96%, Tianjin Guangcheng Chemical Reagent Co., Ltd.), glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$)

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0928-4931/$ – see front matter.
doi:10.1016/j.msec.2010.03.010

(Tianjin Bodi Chemical Co., Ltd.) and yeasts (Instant dry yeast, Angel Yeast Co., Ltd.) have been used. All the aqueous solutions were prepared with distilled water. All reagents were of analytical reagent grade.

2.2. Preparation of Cu_2O hollow spheres

In a typical synthesis procedure, 0.2 g instant dry yeasts were incubated in an aqueous solution of glucose (2 wt.%, 100 mL) at room temperature for 30 min. Then 100 mL of a 0.1 M $CuSO_4$ solution and 100 mL of a 0.2 M NaOH solution were added to the yeast cells solution in sequence under constant magnetic stirring at room temperature. The obtained blue mixture was stirred for 2 h in order to complete the deposition of the product on the surface of yeast cells, and then heated in a water bath. When the temperature reached 50 °C, 100 mL of a 0.1 M glucose solution was gradually added to the mixture drop by drop. After the color turned to brick red, the solution was kept at 50 °C for another 1 h and aged for 12 h. The resulting deposition was recovered by centrifugation at a rotation speed of 4500 rpm, washed five times with distilled water and washed three times with ethanol. The resultant product was dried at 60 °C for 24 h. The control sample without yeast cells was prepared by using a similar process.

2.3. Characterization of samples

The morphology of cultured yeast cells and biotemplated samples were observed by a biological microscope of ECLiPSE80i. The crystal phase composition of the biotemplated sample was determined from XRD patterns recorded using a PANalytical X'Pert PRO X-ray diffractometer with Cu K_α radiation ($\lambda = 0.15418$ nm) in the 2θ range from 10° to 90° with 0.02° min^{-1}. SEM images of the samples were collected by a Quanta 200 scanning electron microscope with accelerating voltage of 20 kV. UV–vis absorption spectrum was recorded on a Shimadzu UV–1700 ultraviolet–visible spectrophotometer.

3. Results and discussion

The X-ray diffraction (XRD) pattern of the biotemplated sample shown in Fig. 1, reveals that all the peaks correspond to the reflections from (110), (111), (200), (211), (220), (311) and (222) planes of cubic Cu_2O, which are consistent with the standard reported values (JCPDS File no.05-0667). The lattice parameter calculated by using Jade 5.0 software is 4.264 Å, which is consistent with the standard value 4.269 Å. No characteristic peak from impurity is detected, indicating that the product is pure Cu_2O. The pure crystal phase is ascribed to the existence of glucose in the process of preparation. Because glucose is a weak reducing agent, only in a strongly basic solution can the Cu^{2+} be reduced to Cu^{+}. The chemical reactions can be divided into three stages:

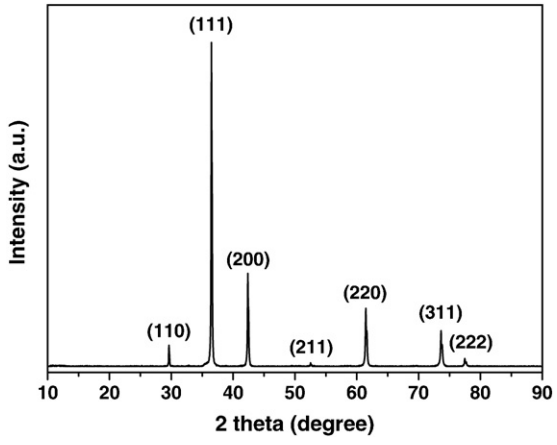

Fig. 1. XRD pattern of as-prepared Cu_2O hollow sphere.

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2\downarrow \quad (1a)$$

$$Cu(OH)_2 + 2OH^- \rightarrow Cu(OH)_4^{2-} \quad (1b)$$

$$2Cu(OH)_4^{2-} + C_6H_{12}O_6 \xrightarrow[\Delta]{50^\circ C} Cu_2O\downarrow + 3OH^- + C_5H_{11}O_5COO^- + 3H_2O \quad (1c)$$

The crystallite size can be estimated to be about 59.5 nm from the line broadening of the (111) peak by Scherrer equation [28]:

$$D_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta} \quad (2)$$

where D_{hkl} is the mean crystallite size, λ is the wavelength of X-ray radiation (Cu K_α radiation, $\lambda = 0.15418$ nm), k is the shape factor and usually taken as 0.896, β_{hkl} is the full width at half maximum (FWHM), after subtraction of equipment broadening, and θ is the Bragg angle.

To investigate morphology of yeast cells and biotemplated samples, SEM and biomicrosopy were utilized. Fig. 2A shows a biomicroscopic image of yeast cells, which reveals that the morphology of yeast cells is approximately spherical with the diameter of about 1.5 μm. Fig. 2B–D shows SEM images of the biotemplated Cu_2O spheres under different regions. Fig. 2B exhibits a clear view of the as-prepared Cu_2O spheres. It can be seen that the average diameter of the spheres is about 1.8 μm. SEM image (Fig. 2C and D inset) provides an evidence of Cu_2O hollow spheres since there are bowl-like broken hollow spheres. SEM image (Fig. 2E) reveals that two special spheres are interconnected to different extents (S1 and S2). The sphere S1 has a smaller protuberance, and sphere S2 possesses twins-like structure. It is likely that yeast cells with proliferation induce Cu_2O particles to form the special structure. The structure is often found during SEM observation. In order to obtain more detailed information, another twins-like hollow sphere is shown in Fig. 2F. The high magnification image shown in Fig. 2G reveals that the peripheral surface is rough and formed by the interconnected nanocrystals. Fig. 2H shows SEM image of the control sample without yeast cells, which reveals that the Cu_2O particles exhibit octahedral-like morphology with the diameter of about 1.5 μm. A comparison of the two above-mentioned samples indicates that yeast cells play important roles in the formation of hollow Cu_2O.

Fig. 3 shows biomicroscopic images of yeast and yeast/Cu_2O at different reaction times. Yeasts are ubiquitous unicellular microorganisms [29]. Yeasts possess a negative surface charge under physiological conditions due to the presence of anionic carboxyl and phosphate groups. Cell surface charge plays an important role in the interaction between cells and metal ions [30]. Fig. 3A and D shows images of yeast cell and yeast cells with proliferation. Fig. 3B and E reveals that Cu_2O particles are formed on the surface of yeast cells after 20 min. The yeast cells are enclosed by Cu_2O particles after 1 h, which is shown in Fig. 3C and F. The process suggests that yeast cells can effectively regulate in situ mineralization on the surface of cells.

According to above result, a schematic illustration of a possible mechanism for the formation of Cu_2O hollow sphere is shown in Fig. 4. In Fig. 4, A and B represent, respectively, yeast cells with no proliferation and proliferation. In the first-step, Cu^{2+} is added to the solution of yeast cells, yeast cells rapidly bind Cu^{2+} through Coulomb interactions between the negative charged functional groups on the cell walls and Cu^{2+}. This leads to the formation of yeast/Cu^{2+} core–shell spheres.